3/Claim for Priority 3-31-01 3

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: HAGIWARA, et al.

Filed: January 14, 2000

For: PATTERN FORMING PROCESS USING PHOTOSENSITIVE RESIN COMPOUND

JC135 U.S. PTO 09/482859 01/14/00

CLAIM FOR PRIORITY

Assistant Commissioner for Patents
Washington, D.C. 20231

January 14, 2000

Sir:

Under the provisions of 35 USC §119 and 37 CFR §1.55, Applicants hereby claim the right of priority based on Japanese Patent Application No. 5/219720, filed September 3, 1993, and No. 6-002282, filed January 14, 1994, each in Japan.

Certified copies of the above-referred-to Japanese Patent Applications were filed on November 2, 1994, in prior application Serial No. 08/299,628, filed September 2, 1994.

Respectfully submitted,

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

DECLARATION OF ACCURACY OF TRANSLATION
IN LIEU OF SWORN TRANSLATION (37 C.F.R. 1.55 & 1.68)

The undersigned translator, Toshio Shimizu of TSUKUNI & ASSOCIATES having an office at 1-22-12, Toranomon, Minato-ku, Tokyo, Japan certifies and declares that:

(1) I am fully conversant both with the Japanese and English languages.

(2) I have carefully compared the attached English language translation of Japanese Patent Application Number 219720/1993, filed September 3, 1993 with the original Japanese-language patent application.

(3) The translation is, to the best of my knowledge, and belief, an accurate translation from the original into the English language.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the matter with which this translation is used.

Date: June 29, 2000 Toshio Shimizu

Toshio Shimizu

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: September 3, 1993

Application Number: Patent Application No. 219720/1993

Applicant(s): HITACHI CHEMICAL CO., LTD.

September 16, 1994

Commissioner,
Patent Office: Akira Takashima
(Sealed)

Certificate No.: Certificate Pat. Hei 06-3047035

[Document name]	Application for patent
[Reference number]	05102000
[Date of submission]	September 3, 1993
[Addressee]	Commissioner, Patent Office, Esq.
[International patent classification]	G03F 7/033
[Title of the invention]	Photosensitive resin composition
[Number of claim(s)]	8
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[Prepayment register number]	010043
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[Document name] Abstract	1
[General authorization number]	9005990
[Proof] Required	

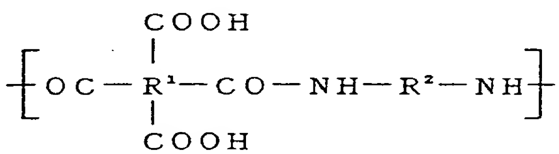
[Document name] Specification

[Title of the invention] Photosensitive resin composition

[Scope of claim for patent]

[Claim 1] A photosensitive resin composition which comprises (A) a polyamic acid having a recurring unit represented by the formula (I):

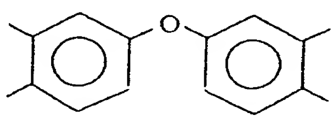
[Structure 1]



(I)

(wherein R^1 represents

[Structure 2]



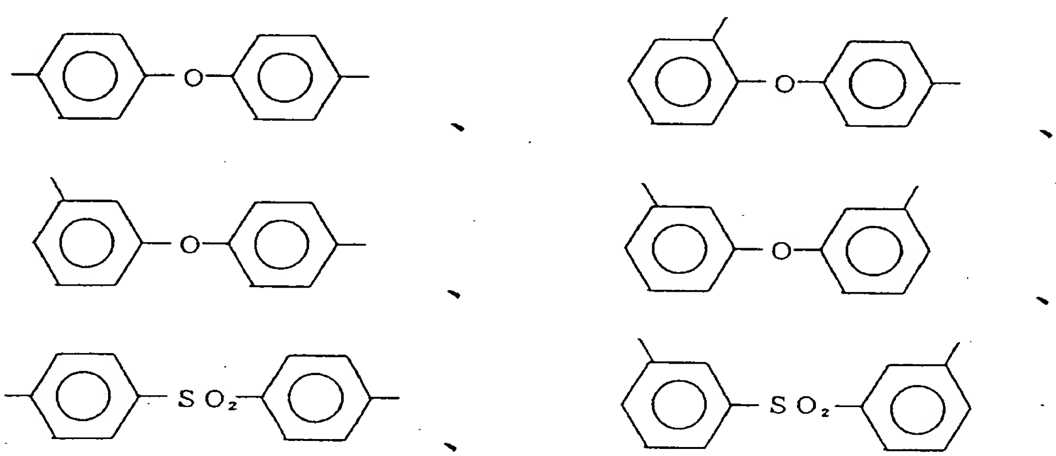
and R^2 represents a divalent organic group),

and

(B) an acryl compound having an amino group.

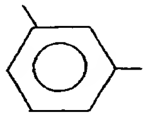
[Claim 2] The photosensitive resin composition according to Claim 1, wherein R^2 in the formula (I) is a group selected from the group consisting of

[Structure 3]

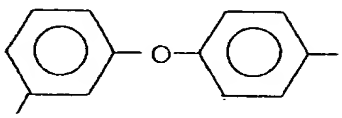


and

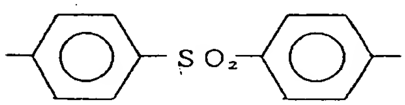
[Structure 4]



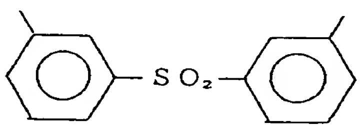
[Claim 3] The photosensitive resin composition according to Claim 1, wherein R^2 in the formula (I) is [Structure 5]



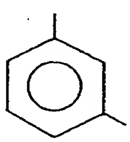
[Claim 4] The photosensitive resin composition according to Claim 1, wherein R^2 in the formula (I) is [Structure 6]



[Claim 5] The photosensitive resin composition according to Claim 1, wherein R^2 in the formula (I) is [Structure 7]



[Claim 6] The photosensitive resin composition according to Claim 1, wherein R^2 in the formula (I) is [Structure 8]



[Claim 7] A photosensitive resin composition which comprises a polyamic acid having the recurring unit shown in Claims 1, 2, 3, 4, 5 and 6, an acryl compound having an amino group and a photoinitiator.

[Claim 8] A photosensitive resin composition which comprises a polyamic acid having the recurring unit shown in Claims 1, 2, 3, 4, 5 and 6, an acryl compound having an amino group, a photoinitiator and an azido compound.

[Detailed description of the invention]

[0001]

[Utilizable field in industry]

This invention relates to a photosensitive resin composition.

[0002]

[Prior art]

In recent years, in the semiconductor industries, as materials for interlaminar insulation which have been conventionally prepared by using inorganic materials, organic materials having an excellent heat-resistance such as a polyimide resin, etc. have primarily been put to use because of properties thereof.

[0003]

Formation of a circuit pattern on a semiconductor integrated circuit or a print substrate is carried out through complex and various steps such as film formation of a resist material on a substrate surface, exposure of required portion to light, removal of unnecessary portion by etching or the like, operation of washing the substrate surface, etc. Therefore, development of heat-resistant photosensitive materials has been desired, which enables the required portion of the resist to be remained as such and used as insulating materials even after the pattern is formed by exposure to light and development.

As these materials, heat-resistant photosensitive materials comprising, for example, a photosensitive poly-imide, a cyclized polybutadiene or the like as a base polymer have been proposed. The photosensitive polyimide has particularly attracted attentions since it has an excellent heat-resistance, impurities can easily be removed, etc.

As such a photosensitive polyimide, for example, a system which comprises a polyimide precursor and a bi-chromate has been proposed for the first time in Japanese Patent Publication No. 17374/1974. This material has an advantage that it has a photosensitivity suitable for practical uses and also has a high film-forming ability,

etc. However, it also has a disadvantage that it has a low storage stability and that a chromium ion remains in the polyimide, and therefore it has not been put to practical use.

As another example, a photosensitive polyimide precursor in which a photosensitive group is introduced into a polyamic acid (polyimide precursor) by an ester bond has been proposed in Japanese Patent Publication No. 30207/1980. This material has a problem that a chloride remains finally since a step for introducing the photosensitive group comprises a dehydrochlorination reaction.

[0004]

In order to avoid these problems, for example, a process for mixing a compound having a photosensitive group with a polyimide precursor has been proposed in Japanese Provisional Patent Publication No. 109828/1979, and a process for affording a photosensitivity by reacting a functional group in a polyimide precursor with a functional group of a compound having a photosensitive group has been proposed in Japanese Provisional Patent Publication No. 24343/1981, Japanese Provisional Patent Publication No. 100143/1985, etc.

However, these photosensitive polyimide precursors employ an aromatic polyimide having excellent heat-resistance and mechanical property as a fundamental skeleton and has a low light-transmittance in the ultraviolet region because of absorption by the polyimide itself. Therefore, photochemical reactions at the exposed portion cannot sufficiently and effectively be caused, which results in problems such as a low sensitivity and worsening of pattern shapes.

In particular, recently, a wavelength of light to be used for exposure is made a shorter wavelength (i-line: 365 nm) accompanied by enlargement in size of silicon wafers. A low light-transmittance of a base polymer of the photosensitive polyimide precursors is a more serious problem.

[0005]

[Task to be solved by the invention]

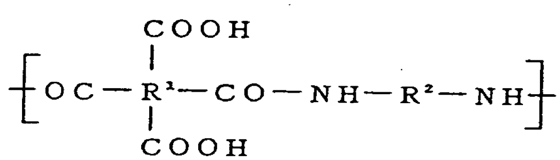
The present invention has been made in consideration of the problems as described above and it is an object thereof to provide a photosensitive resin composition which transmits light to be used for exposure sufficiently and has excellent film property, heat-resistance, adhesive property, image-forming ability, etc.

[0006]

[Means for solving the task]

The present invention relates to a photosensitive resin composition which comprises (A) a polyamic acid having a recurring unit represented by the formula (I):

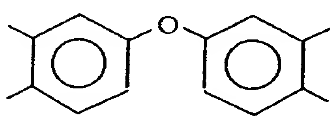
[Structure 9]



(I)

(wherein R^1 represents

[Structure 10]



and R^2 represents a divalent organic group), and

(B) an acryl compound having an amino group.

[0007]

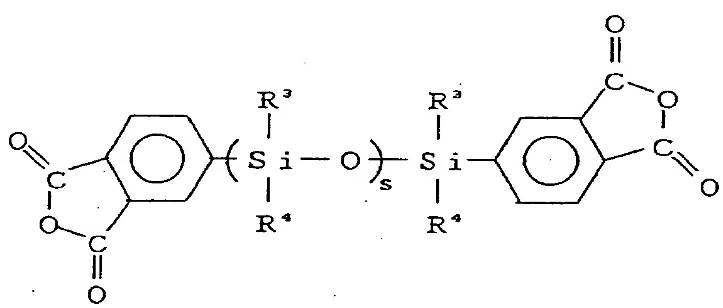
The polyamic acid (A) in the present invention can be obtained, for example, by carrying out a polycondensation reaction of an acid component comprising oxydiphthalic acid or oxydiphthalic anhydride and other tetracarboxylic dianhydride which may be used, if necessary, with a diamine in an organic solvent.

[0008]

As the above other tetracarboxylic dianhydride which may be used, if necessary, there may be mentioned, for example, an aromatic tetracarboxylic anhydride such as

pyrromellitic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 2,3,5,6-pyridinetetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 3,4,9,10-perylenetetracarboxylic dianhydride, sulfonyldiphthalic anhydride, m-terphenyl-3,3',4,4'-tetracarboxylic dianhydride, p-terphenyl-3,3',4,4'-tetracarboxylic dianhydride, 1,1,1,3,3,3-hexafluoro-2,2-bis(2,3- or 3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(2,3- or 3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis{4,(2,3- or 3,4-dicarboxyphenoxy)-phenyl}propane dianhydride, 1,1,1,3,3,3-hexafluoro-2,2-bis{4-(2,3- or 3,4-dicarboxyphenoxy)phenyl}propane dianhydride, a tetracarboxylic anhydride represented by the following formula (II):

[Structure 11]



(II)

(wherein R^3 and R^4 each represent a monovalent hydrocarbon group and may be the same or different, and s is an integer of 1 or more), etc. These may be used singly or in combination of two or more.

[0009]

These tetracarboxylic dianhydrides may be used, if necessary, in addition to oxydiphthalic anhydride which is an essential component. The amount thereof to be used is preferably such an amount that the light-transmittance of the resulting polyamic acid is not lowered, and they are preferably used in an amount of 80 mol % or less based on the whole acid component.

[0010]

As the above diamine, which is not particularly limited, there may be preferred 4,4'-diaminodiphenyl ether, 2,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone and metaphenylenediamine. These may be used singly or in combination of two or more.

[0011]

In addition to these diamines, there may be used with an amount which does not lower the light-transmittance of the resulting polyimide precursor, for example, p-phenylenediamine, p-xylylenediamine, 1,5-diaminonaphthalene, 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine, 4,4'- (or 3,4'-, 3,3'-, 2,4'-, 2,2'-)diaminodiphenylmethane, 2,2'-diaminodiphenyl ether, 3,4'- (or 2,4'-, 2,2'-)diaminodiphenyl sulfone, 4,4'- (or 3,4'-, 3,3'-, 2,4'-, 2,2'-)-diaminodiphenylsulfide, 4,4'-benzophenonediamine, bis{4-(4'-aminophenoxy)phenyl}sulfone, 1,1,1,3,3,3-hexafluoro-2,2-bis(4-aminophenyl)propane, 2,2-bis{4-(4'-aminophenoxy)-phenyl}propane, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane, bis{4-(3'-aminophenoxy)phenyl}sulfone, 2,2-bis(4-aminophenyl)-propane and an aliphatic diamine such as a diaminopolysiloxane represented by the following formula (III):

[Structure 12]

$$H_2N-R^5\left(\begin{matrix}R^7\\|\\Si\\|\\R^8\end{matrix}-O\right)_t\begin{matrix}R^7\\|\\Si\\|\\R^8\end{matrix}-R^6-NH_2 \qquad \text{(III)}$$

(wherein R^5 and R^6 each represent a divalent hydrocarbon group, R^7 and R^8 each represent a monovalent hydrocarbon group, R^5, R^6, R^7 and R^8 may be the same or different, and t is an integer of 1 or more), etc.

[0012]

There may be also used a hydroxyl group-containing diamine such as 3,3'-hydroxybenzidine, 3,4'-diamino-3',4-

dihydroxybiphenyl, 3,3'-dihydroxy-4,4'-diaminodiphenyl-oxide, 3,3'-dihydroxy-4,4'-diaminodiphenylsulfone, 2,2-bis(3-amino-4-hydroxyphenyl)propane, 1,1,1,3,3,3-hexa-fluoro-2,2-bis-(3-amino-4-hydroxyphenyl)propane, bis-(3-hydroxy-4-aminophenyl)methane, 3,3'-dihydroxy-4,4'-diaminobenzophenone, 1,1-bis(3-hydroxy-4-aminophenyl)-ethane, 2,2-bis-(3-hydroxy-4-aminophenyl)propane, 1,1,1,3,3,3-hexafluoro-2,2-bis-(3-hydroxy-4-aminophenyl)-propane, 1,3-diamino-4-hydroxybenzene, 1,3-diamino-5-hydroxybenzene, 1,3-diamino-4,6-dihydroxybenzene, 1,4-diamino-2-hydroxybenzene, 1,4-diamino-2,5-dihydroxybenzene, etc. These may be used singly or in combination of two or more.

[0013]

As the organic solvent to be used for the above reaction, a polar solvent which completely dissolves the formed polyimide precursor is generally preferred. There may be mentioned, for example, N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, dimethylsulfoxide, tetramethylurea, hexamethylphosphoric acid triamide, γ-butyrolactone, etc.

[0014]

In addition to this polar solvent, there may be also used ketones, esters, lactones, ethers, halogenated hydrocarbons, hydrocarbons, for example, acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, methyl acetate, ethyl acetate, butyl acetate, diethyl oxalate, diethyl malonate, diethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetrahydrofuran, dichloromethane, 1,2-dichloroethane, 1,4-dichlorobutane, trichloroethane, chlorobenzene, o-dichlorobenzene, hexane, heptane, octane, benzene, toluene, xylene, etc.

These organic solvents may be used singly or in combination of two or more.

[0015]

As the acryl compound having an amino group (B) to be used in the present invention, there may be mentioned, for

example, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, N,N-dimethylaminopropyl methacrylate, N,N-diethylaminopropyl methacrylate, N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, N,N-dimethylaminopropyl acrylate, N,N-diethylaminopropyl acrylate, N,N-dimethylaminoethylacrylamide, N,N-dimethylaminoethylacrylamide, etc. These may be used singly or in combination of two or more.

[0016]

The amount of the acryl compound having an amino group (B) to be used is preferably 1 to 200 % by weight, more preferably 5 to 50 % by weight based on the polyamic acid (A) having the recurring unit represented by the formula (I) from the points of photosensitivity, the heat-resistance film strength , etc.

[0017]

The photosensitive resin composition of the present invention may contain, if necessary, (C) a photoinitiator as shown below. As the photoinitiator (C), there may be mentioned, for example, Michler's ketone, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, 2-t-butylanthraquinone, 2-ethylanthraquinone, 4,4'-bis(diethylamino)benzophenone, acetophenone, benzophenone, thioxanthone, 2,2-dimethoxy-2-phenylacetophenone, 1-hydroxycyclohexyl phenyl ketone, 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propanone, benzil, diphenyldisulfide, phenanthrenequinone, 2-isopropylthioxanthone, riboflavin tetrabutyrate, 2,6-bis(p-diethylaminobenzal)-4-methyl-4-azacyclohexanone, N-ethyl-N-(p-chlorophenyl)glycine, N-ethyl-N-(p-chlorophenyl)glycine, N-phenyldiethanolamine, 2-(o-ethoxycarbonyl)oxyimino-1,3-diphenylpropanedione, 1-phenyl-2-(o-ethoxycarbonyl)oxyiminopropan-1-one, 3,3',4,4'-tetra-(t-butylperoxycarbonyl)benzophenone, 3,3'-carbonylbis(7-diethylaminocoumarin), etc. These may be used singly or in combination of two or more.

[0018]

When these photoinitiators (C) are used, the amount thereof to be used is preferably 0.01 to 30 % by weight, more preferably 0.05 to 10 % by weight based on the polyamic acid (A) having the recurring unit represented by the formula (I) from the points of photosensitivity, film strength, etc.

[0019]

The photosensitive resin composition of the present invention may contain, if necessary, (D) an addition-polymerizable compound as shown below. As the addition-polymerizable compound (D), there may be mentioned, for example, diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, trimethylolpropane diacrylate, trimethylolpropane triacrylate, trimethylolpropane dimethacrylate, trimethylolpropane trimethacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol methacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, styrene, divinylbenzene, 4-vinyltoluene, 4-vinylpyridine, N-vinylpyrrolidone, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 1,3-acryloyloxy-2-hydroxypropane, 1,3-methacryloyloxy-2-hydroxypropane, methylenebisacrylamide, N,N-dimethylacrylamide, N-methylolacrylamide, etc. These may be used singly or in combination of two or more.

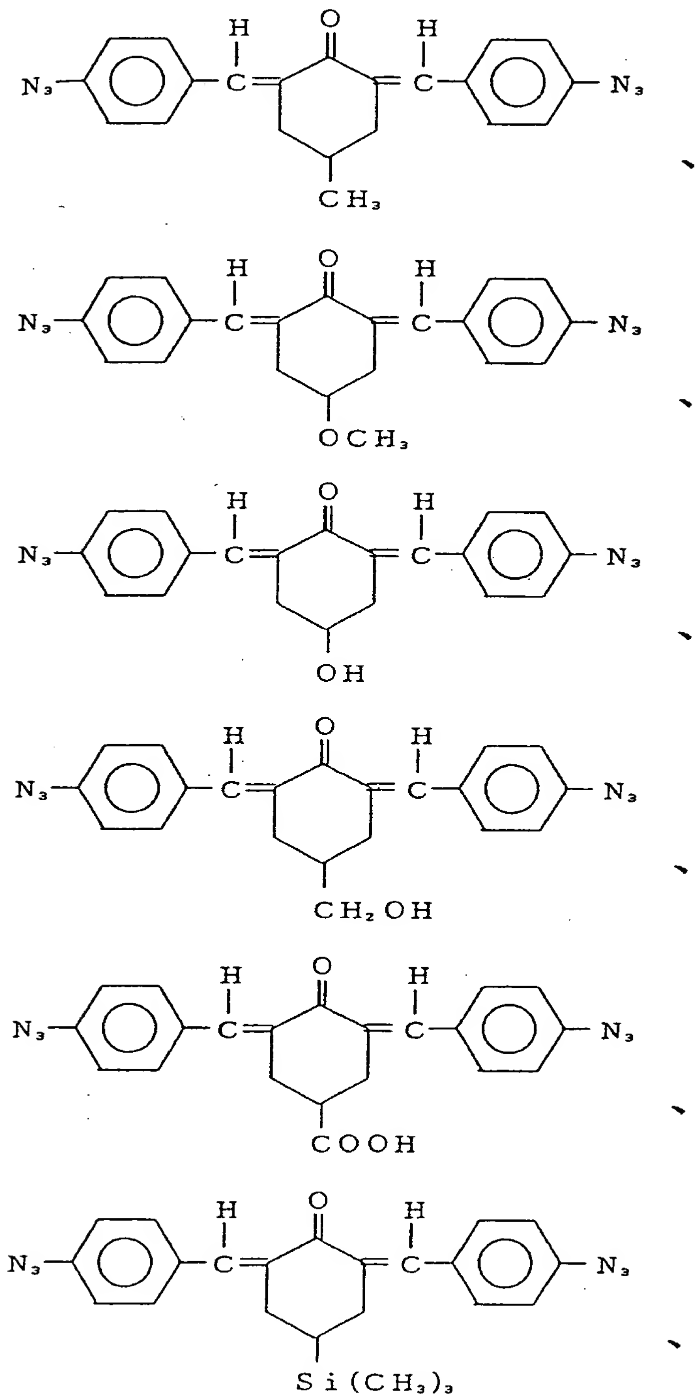
[0020]

When the addition-polymerizable compound (D) is used, the amount thereof to be used is preferably 1 to 200 % by weight based on the polyamic acid having the recurring unit represented by the formula (I) from the points of photosensitive properties including solubility in a developer, film strength, etc.

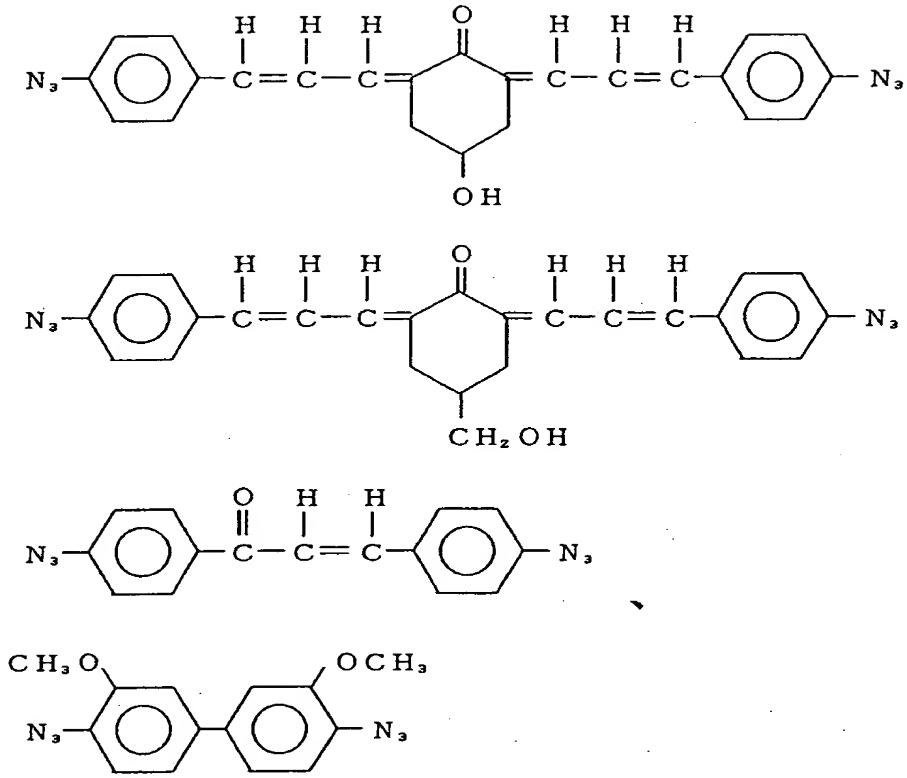
[0021]

The photosensitive resin composition of the present invention may contain, if necessary, (E) an azido compound as shown below. As the azido compound (E), there may be mentioned, for example,

[Structure 13]



[Structure 14]



and the like. These may be used singly or in combination of two or more.

[0022]

When these azido compounds (E) are used, the amount thereof to be used is preferably 0.01 to 30 % by weight, more preferably 0.05 to 10 % by weight based on the poly-amic acid (A) having the recurring unit represented by the formula (I) from the points of photosensitivity, strength of the film, etc.

[0023]

The photosensitive resin composition of the present invention may contain a radical polymerization-inhibiting agent or a radical polymerization-suppressing agent such as p-methoxyphenol, hydroquinone, pyrogallol, phenothiazine, nitrosoamines, etc. for heightening stability during storage.

[0024]

The photosensitive resin composition of the present invention may be applied to a substrate such as a silicon wafer, a metal substrate, a glass substrate, a ceramic substrate, etc. by a dipping method, a spraying method, a screen printing method, a rotary coating method or the like, and then heat-dried to evaporate most of the solvent so that a film having no tackiness can be obtained.

[0025]

Active rays or chemical rays are irradiated on this film through a mask having required patterns. As the active rays or chemical rays to be irradiated, there may be mentioned ultraviolet rays, far-ultraviolet rays, visible light, electron rays, X rays, etc. It is convenient to use ultraviolet rays. The required relief pattern can be obtained by dissolving and removing the non-irradiated portion with an appropriate developer after the irradiation.

[0026]

As the developer, there may be used a good solvent such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, etc., a mixed solvent of the above and a poor solvent such as a lower alcohol, water or an aromatic hydrocarbon, etc., or a basic solution such as tetramethylammonium hydroxide aqueous solution, triethanolamine aqueous solution, etc. After the development, the film is rinsed with water or a poor solvent and dried at around 100 °C so that the pattern is stabilized. In order to afford heat-resistance to this relief pattern, the relief pattern is heated at a temperature of 200 to 500 °C, preferably 300 to 400 °C for several tens of minutes to several hours to form a highly heat-resistant polyimide having patterns.

[0027]

The photosensitive resin composition of the present invention can be thus converted to a buffer coating film of a semiconductor, an interlaminar insulating film of a multi-layer wiring board, etc.

[0028]

[Examples]

In the following, the present invention is described in detail by referring to Examples.

[0029]

Synthetic example 1

To a 100 ml-flask equipped with a stirrer, a thermometer and an inlet for introducing nitrogen were added 9.8917 g of 3,4'-diaminodiphenyl ether, 0.6462 g of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, 2.2484 g of water, 14.60 g of xylene and 58.38 g of N-methyl-2-pyrrolidone and the mixture was dissolved by stirring under nitrogen flow at room temperature. Then, 16.4534 g of oxydiphthalic anhydride was added to this solution and the mixture was stirred for 5 hours to obtain a tacky polyamic acid (polyimide precursor) solution. Further, this solution was heated at 70 °C for adjusting the viscosity at 80 poise. This polymer solution is called as P-1.

[0030]

Synthetic example 2

To a 500 ml-flask equipped with a stirrer, a thermometer and an inlet for introducing nitrogen were added 49.4583 g of 2,4'-diaminodiphenyl ether, 3.2308 g of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, 72.10 g of xylene and 288.42 g of N-methyl-2-pyrrolidone and the mixture was dissolved by stirring under nitrogen flow at room temperature. Then, 80.6541 g of oxydiphthalic anhydride was added to this solution and the mixture was stirred for 5 hours to obtain a tacky polyamic acid (polyimide precursor) solution. Further, this solution was heated at 70 °C for adjusting the viscosity at 80 poise. This polymer solution is called as P-2.

[0031]

Synthetic example 3

To a 500 ml-flask equipped with a stirrer, a thermometer and an inlet for introducing nitrogen were added 57.0855 g of 3,3'-diaminodiphenylsulfone, 3.0071 g of 1,3-

bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, 73.09 g of xylene and 292.35 g of N-methyl-2-pyrrolidone and the mixture was dissolved by stirring under nitrogen flow at room temperature. Then, 75.0703 g of oxydiphthalic anhydride was added to this solution and the mixture was stirred for 5 hours to obtain a tacky polyamic acid (polyimide precursor) solution. Further, this solution was heated at 70 °C for adjusting the viscosity at 80 poise. This polymer solution is called as P-3.

【0032】

Synthetic example 4

To a 500 ml-flask equipped with a stirrer, a thermometer and an inlet for introducing nitrogen were added 57.0855 g of 4,4'-diaminodiphenylsulfone, 3.0071 g of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, 73.09 g of xylene and 292.35 g of N-methyl-2-pyrrolidone and the mixture was dissolved by stirring under nitrogen flow at room temperature. Then, 75.0703 g of oxydiphthalic anhydride was added to this solution and the mixture was stirred for 5 hours to obtain a tacky polyamic acid (polyimide precursor) solution. Further, this solution was heated at 70 °C for adjusting the viscosity at 80 poise. This polymer solution is called as P-4.

【0033】

Synthetic example 5

To a 100 ml-flask equipped with a stirrer, a thermometer and an inlet for introducing nitrogen were added 6.3697 g of methaphenylenediamine, 0.7704 g of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, 2.6808 g of water, 14.47 g of xylene and 57.88 g of N-methyl-2-pyrrolidone and the mixture was dissolved by stirring under nitrogen flow at room temperature. Then, 19.6176 g of oxydiphthalic anhydride was added to this solution and the mixture was stirred for 5 hours to obtain a tacky polyamic acid (polyimide precursor) solution. Further, this solution was heated at 70 °C for adjusting the viscosity at 80 poise. This polymer solution is called as P-5.

[0034]

Synthetic example 6

To a 200 ml-flask equipped with a stirrer, a thermometer and an inlet for introducing nitrogen were added 19.5931 g of 4,4'-diaminodiphenyl ether, 1.2799 g of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, 4.4536 g of water, 29.26 g of γ-butyrolactone and 117.02 g of N-methyl-2-pyrrolidone and the mixture was dissolved by stirring under nitrogen flow at room temperature. Then, 33.2295 g of oxydiphthalic anhydride was added to this solution and the mixture was stirred for 5 hours to obtain a polyamic acid (polyimide precursor) solution. Further, this solution was heated at 70 °C for adjusting the viscosity at 80 poise. This polymer solution is called as P-6.

[0035]

Synthetic example 7

To a 100 ml-flask equipped with a stirrer, a thermometer and an inlet for introducing nitrogen were added 11.9841 g of 4,4'-diaminodiphenyl ether, 0.7829 g of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, 2.7240 g of water, 14.48 g of xylene and 57.93 g of N-methyl-2-pyrrolidone and the mixture was dissolved by stirring under nitrogen flow at room temperature. Then, 14.0161 g of pyromellitic dianhydride was added to this solution and the mixture was stirred for 5 hours to obtain a tacky polyamic acid (polyimide precursor) solution. Further, this solution was heated at 70 °C for adjusting the viscosity at 80 poise. This polymer solution is called as P-7.

[0036]

Synthetic example 8

To a 100 ml-flask equipped with a stirrer, a thermometer and an inlet for introducing nitrogen were added 10.0819 g of 4,4'-diaminodiphenyl ether, 0.6586 g of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, 2.2916 g of water, 14.41 g of xylene and 90.05 g of N-methyl-2-pyrrolidone and the mixture was dissolved by stirring under nitrogen flow at room temperature. Then, 15.9049 g of

biphenyltetracarboxylic dianhydride was added to this solution and the mixture was stirred for 5 hours to obtain a polyamic acid (polyimide precursor) solution. Further, this solution was heated at 70 °C for adjusting the viscosity at 80 poise. This polymer solution is called as P-8.

[0037]

The transmittance at 365 nm of the polyamic acid (polyimide precursor) solutions P-1 to P-8 obtained in Synthetic examples 1 to 8, in a film state are shown in Table 1. The transmittance of the polyamic acid was determined by measuring a film obtained by spin-coating a glass substrate with the resin solution of the polyamic acid (polyimide precursor) and drying it at 85 °C for 3 minutes and further at 105 °C for 3 minutes, by using a spectrophotometer.

[0036]

[Table 1]

Table 1

	Polyamic acid solution	Light transmittance (film thickness: 20 μm, at 365 nm) (%)
Synthetic example 1	PI-1	43
Synthetic example 2	PI-2	48
Synthetic example 3	PI-3	68
Synthetic example 4	PI-4	60
Synthetic example 5	PI-5	62
Synthetic example 6	PI-6	40
Synthetic example 7	PI-7	less than 1
Synthetic example 8	PI-8	less than 1

[0039]

Examples 1 to 6

To each 10 g of the polyamic acid (polyimide precursor) solutions P-1 to P-6 obtained in Synthetic examples 1 to 6 were added MDAP, CA, EAB and PDO in a prescribed amount as shown in Table 2 and were mixed while stirring to

obtain uniform photosensitive resin composition solutions which were to be used in Examples 1 to 6.

[0040]

Comparative examples 1 and 2

To each 10 g of the polyamic acid (polyimide precursor) solutions P-7 and P-8 obtained in Synthetic examples 7 and 8 were added MDAP, CA, EAB and PDO in a prescribed amount as shown in Table 2 and were mixed while stirring to obtain uniform photosensitive resin composition solutions which were to be used in Comparative examples 1 and 2.

[0041]

[Table 2]

Table 2

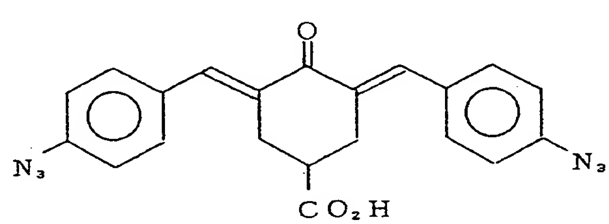
	Polyamic acid solution	Formulation (g)			
		MDAP	CA	EAB	PDO
Example 1	PI-1	1.803	0.027	0.027	0.054
Example 2	PI-2	1.803	0.027	0.027	0.054
Example 3	PI-3	1.656	0.027	0.027	0.054
Example 4	PI-4	1.656	0.027	0.027	0.054
Example 5	PI-5	2.174	0.027	0.027	0.054
Example 6	PI-6	1.803	0.027	0.027	0.054
Comparative example 1	PI-7	2.198	0.027	0.027	0.054
Comparative example 2	PI-8	1.861	0.027	0.027	0.054

[0042]

[Structure 15]

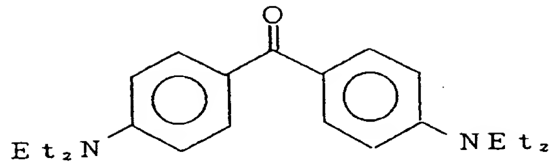
MDAP $CH_2=C(CH_3)CO_2(CH_2)_3N(CH_3)_2$

CA



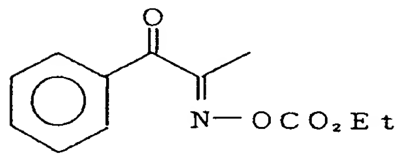
2,6-bis(4'-azidobenzal)-4-carboxycyclohexanone

EAB



4,4'-bis(diethylamino)benzophenone

PDO



1-phenyl-2-(O-ethoxycarbonyl)oxyiminopropan-1-one

[0043]

Each of these solutions was filtered and was drip spin-coated on a silicon wafer, respectively. Next, the wafer was heated at 100 °C for 150 seconds by using a hot plate to form a film having a thickness of 20 μm and the film was exposed to light by using an i-line stepper through a mask having patterns. This film was further heated at 110 °C for 50 seconds and subjected to puddle development using a mixed solution comprising N-methyl-2-pyrrolidone/water (weight ratio: 75/25). This film was heated at 100 °C for 30 minutes, at 200 °C for 30 minutes and at 350 °C for 60 minutes under nitrogen atmosphere to obtain the relief pattern of the polyimide.

[0044]

Evaluation results thereof are shown in Table 3. The resolution, the post-developmental film-remaining ratio and the adhesive property were evaluated by using methods as mentioned below.

[0045]

The resolution was evaluated as the minimal size of developable through-hole by using a through-hole test pattern.

[0046]

The post-developmental film-remaining ratio was determined as (the film thickness after development/the film thickness before development) x 100 (%) by measuring the film thicknesses before the development and after the development. The film thickness was measured with a film thickness measurement apparatus, Dektak-3030 manufactured by Sloan Co.

[0047]

The adhesive property was evaluated by a checkerboard test after a film (film thickness: 5 μm) obtained by coating the photosensitive resin composition on a silicon wafer and heating it at 100 °C for 30 minutes, at 200 ° C for 30 minutes and at 350 °C for 60 minutes under nitrogen atmosphere was subjected to a Pressure Cooker test (conditions: at 121 °C, 2 atmospheric pressure for 100 hours).

[0048]

The checkerboard test is a method in which a film is cut like a checkerboard by a knife so that 100 squares with 1 mm are formed and peeled off by using a cellophane tape regulated by JIS (JIS K5400) to determine the number of remaining squares to 100 squares.

[0049]

[Table 3]

Table 3

	Resolution (μm)	Pattern shape	Post-developmental film-remaining ratio (%)	Adhesive property
Example 1	10	Good	95	100/100
Example 2	10	Good	97	100/100
Example 3	10	Good	94	100/100
Example 4	10	Good	96	100/100
Example 5	10	Good	96	100/100
Example 6	10	Good	98	100/100
Comparative Example 1	-	Poor	-	100/100
Comparative Example 2	-	Poor	-	100/100

[0050]

[Effect of the invention]

The photosensitive resin composition of the present invention uses a polyamic acid having excellent light-transmittance so that it is excellent in image-forming ability and particularly suitable for pattern-formation with an i-line. The polyimide obtained therefrom is also excellent in mechanical properties, heat-resistance, adhesive property, etc. of the film.

[Document name] Abstract

[Summary]

[Object] It is to provide a photosensitive resin composition which has good light-transmittance and has excellent film property, heat-resistance, adhesive property, image-forming ability, etc.

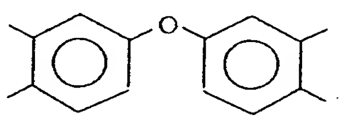
[Constitution] A photosensitive resin composition which comprises (A) a polyamic acid having a recurring unit represented by the formula (I):

[Structure 1]

$$\left[OC - \underset{\substack{| \\ COOH}}{\overset{\substack{COOH \\ |}}{R^1}} - CO - NH - R^2 - NH \right] \qquad (I)$$

(wherein R^1 represents

[Structure 2]



and R^2 represents a divalent organic group),

and

(B) an acryl compound having an amino group.

[Selective drawing] None

[Document name] Official competent correction data
[Document to be corrected] Application for patent

<Recognized information·additional information>
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